

## PRELIMINARY PROPERTIES OF A RESIN FROM ETHYNYL TERMINATED MATERIALS

Paul M. Hergenrother and John W. Connell  
Materials Division  
NASA Langley Research Center  
Hampton, VA

## SUMMARY

A blend composed of an ethynyl terminated aspartimide (brittle component) and an ethynyl terminated arylene ether oligomer (tough component) was thermally cured to yield a resin which underwent preliminary evaluation to determine the potential for use in structural applications on aerospace vehicles. The blend exhibited good compression moldability, allowing for the fabrication of neat resin moldings, adhesive specimens and composites at temperatures of 250°C under a pressure of [1.4 MPa (200 psi)]. Neat resin moldings and adhesive specimens provided relatively high mechanical properties. Composite specimens provided promising results in spite of fiber misalignment, fiber washout and a small amount of panel warpage.

## INTRODUCTION

As part of a NASA program to develop technology on high performance/high temperature structural resins, particularly composite matrices, the chemistry and properties of blends of ethynyl (acetylenic) terminated materials are under investigation (ref. 1-6). Specifically, low molecular weight diethynyl compounds such as ethynyl terminated aspartimides (ETA), are mixed with ethynyl terminated arylene ether oligomers (ETAE) of different molecular weights. The number average molecular weights ( $M_n$ ) ranged from 3000 to 12,000 g/mole. The ETA served as the brittle thermosetting component while the ETAE was the tough linear component.

Various blends have been prepared and subsequently thermally cured under different conditions to determine the effect of composition and crosslink density on final resin properties. The objective was to obtain materials with good compression moldability and cured neat resins and composites with a favorable combination of mechanical properties at temperatures as high as 177°C. The work reported herein concerns the chemistry and the mechanical and physical properties of one of these blends.

## EXPERIMENTAL

## Ethynyl Terminated Aspartimide

The ethynyl terminated aspartimide was prepared from the reaction of N,N-bismaleimido-4,4'-diphenylmethane and 3-ethynylaniline as previously reported (ref. 1). The aspartimide was obtained in the form of a tan solid as a mixture of d, l and meso stereoisomers, mp 104-110°C.

## Ethynyl Terminated Arylene Ether Oligomer

The ethynyl terminated arylene ether oligomers was prepared following a known procedure (ref. 2) by reacting 4,4'-dichlorobenzophenone with a calculated excess of 9,9-bis(4-hydroxyphenyl)fluorene to afford a hydroxy terminated oligomer with  $M_n$  of ~ 8000 g/mole. The hydroxy terminated oligomer was subsequently end-capped with 4-ethynylbenzoyl chloride. The ETAE oligomer had an inherent viscosity of 0.29 dL/g and initial glass transition ( $T_g$ ) of 238°C. The 300°C cured resin exhibited a  $T_g$  of 248°C.

## Blend

The blend was prepared by dissolving an equal weight of each component in 1,4-dioxane to yield clear solutions. To isolate the blend, the solution was added to water in a high speed blender. The solid was collected, washed with water and stage-dried to 100°C under vacuum. These powders were used to prepare moldings and films. The blend had an initial  $T_g$  of 140°C and the cured resin exhibited a  $T_g$  of 245°C, fracture toughness ( $K_{IC}$ ) of [1.57 MPa m<sup>1/2</sup> (1425 psi in<sup>1/2</sup>)] and a coefficient of thermal expansion (23 to 200°C) of 36.8 ppm/°C.

## Films

Thin films [approximately 0.127 mm (5 mils thick)] of the blend were prepared by melt pressing powders of the blend at [6.7 to 10.3 MPa (1 to 1.5 Ksi)] for 0.5 h at 250°C. The film specimens [5.1 cm x 0.63 cm x 0.013 cm (2 in x 0.25 in x 0.005 in)] were bent back upon themselves to place the rounded portion under stress and immersed in hydraulic fluid (Chevron Hyjet IV) for 24 h and in chloroform for 1 h to determine sensitivity towards these solvents.

## Molded Specimens

Powdered blend was compression-molded by heating to 200° and then 250°C, each for 0.5 h under [1.4 MPa (200 psi)] in a stainless steel mold. Miniature compact tension specimens [1.6 cm x 1.6 cm x 0.95 cm thick (0.62 in x 0.62 in x 0.375 in thick)] were machined from the moldings and subsequently tested to determine fracture toughness ( $K_{IC}$ , critical stress intensity factor) according to ASTM E399 using four specimens per test.

Flat moldings [7.6 cm x 7.6 cm x 0.18 cm (3.0 in x 3.0 in x 0.070 in)] were prepared by compression-molding the powdered blend using the conditions described above. Dogbone specimens [6.35 cm x 0.92 cm x 0.18 cm (2.5 in x 0.375 x 0.070 in)] were machined from the moldings and subsequently tested to determine neat resin tensile properties according to ASTM D638 using four specimens per test.

## Adhesive Specimens

Adhesive tape was prepared by multiple coating of 112-E glass (A-1100 finish) with a 1,4-dioxane solution (~ 30% solids content) of the blend and subsequently stage dried to 100°C for 1 h after each coat. The final volatile contents of the tapes were less than 1%. Standard adhesive specimens [bond area 2.54 cm (1.00 in) wide x 1.27 cm (0.5 in) overlap] using titanium (Ti, 6Al-4V) adherends with a Pasa Jell 107 (Products Research and Chemical Corp., Semco Div.) surface treatment were fabricated using conditions similar to those described for the molded specimens. The Ti adherends were initially primed with a dilute 1,4-dioxane solution (~ 5% solid content) of the blend and subsequently dried at 100°C for 1 h. Tensile shear specimens were tested according to ASTM D1002 using four specimens per test condition.

## Composite Specimens

Prepreg was prepared by using a 25% solid solution of the blend in 1,4-dioxane to coat unsized AS-4 (12K tow) carbon/graphite fiber on a drum winding machine. The solutions had Brookfield viscosities of ~ 400 centipoise at 23°C. After drying the prepreg to a final temperature of 100°C for 1 hour, the volatile content was ~ 1% (determined by heating a weighed piece of prepreg for 1 hour at 300°C). Unidirectional and cross-ply laminates were fabricated in a stainless steel mold by heating to 200°C and then 250°C for 0.5 hour each under [1.4 MPa (200 psi)]. In some cases the panels were postcured by heating at 250°C for 2 hours under [1.4 MPa (200 psi)]. After ultrasonic scanning to detect voids, the panels were cut into specimens and tested for various properties according to ASTM procedures. Fracture energy was determined by testing double cantilever beam specimens according to a previously reported method (ref. 7). Tensile, flexural and short beam shear properties were determined according to ASTM D-3518, D-790, and D-2344 respectively.

## Radiation Exposure

Electron beam radiation exposure was performed on composite and neat resin test specimens. The specimens were exposed to 1 MeV electrons using a Radiation Dynamics, Inc., Dynamitron Model 1000/10 accelerator. The samples were mounted side by side on a temperature-controlled aluminum plate positioned in the uniform area of the electron beam. The absorbed dose and dose rate were calculated from current flux levels monitored with a Faraday cup mounted in the exposure area of the aluminum plate. The Faraday cup was calibrated through the use of National Bureau of Standards calibrated polymeric dosimeter films. The exposure chamber operated at a pressure of  $2 \times 10^{-7}$  torr and the temperature of the specimens did not exceed 40°C. The materials received doses of  $5.5 \times 10^8$  rads and  $1.0 \times 10^9$  rads at a dose rate of  $5 \times 10^7$  rads/h without interruption. After exposure the specimens were stored in a desiccator until tested.

## Other Characterization

Differential Scanning Calorimetry (DSC) was performed at a heating rate of 20°C/min with the  $T_g$  taken at the inflection point of the  $\Delta T$  versus temperature curve after heating the sample to 300°C and quenching. Coefficient of thermal expansion (CTE) measurements were performed on a DuPont 9900 Computer/Thermal Analyzer at a heating rate of 5°C/min over the temperature range of 25-200°C using an expansion probe.

## RESULTS AND DISCUSSION

Although a number of different ETAs have been reported (ref. 1), the ETA in figure 1 was selected for this study because of the following factors. It is easy to synthesize and it exhibited a favorable combination of highly desirable processing properties such as low and broad melting range, low melt viscosity, and a wide range between the melting and curing temperatures. In addition, it cures to provide a material with relatively high solvent resistance and tensile modulus.

The ETAE was selected from a variety of candidates on the basis of compatibility with the ETA and providing a cured material with a relatively high  $T_g$ . The blend was readily prepared by dissolving an equal quantity of each component in 1,4-dioxane. A portion of the solution was poured into water to precipitate a solid for characterization and neat resin molding studies. The remaining solution was used to prepare adhesive tape and prepreg.

The initial neat resin properties of the cured blend and those after exposure to various conditions are presented in table 1. The initial properties after a 0.5 hr cure at 250°C under [1.4 MPa (200 psi)] are respectable and suggest that this material should perform well as a composite matrix. The room temperature tensile properties were essentially unchanged after processing for 2 hr at 250°C. The tensile modulus of 3.6 GPa should be adequate to support the composite reinforcement filaments under compressive loading, thereby inhibiting microbuckling of the fibers. Upon exposure, the  $T_g$  and tensile modulus increased with a decrease in the elongation. This is due to further cure that resulted in higher crosslink density.

The  $T_i$  to  $T_i$  tensile shear strengths are given in table 2. The initial strengths at 23 and 150°C are relatively good whereas the initial 177°C value was low, presumably due to inadequate cure. After aging specimens for 650 hr at 200°C in air, further cure occurred that is reflected in a lower 23°C strength and a significantly higher 177°C value. In essence, after exposure for 650 hr at 200°C in air, the 23, 150 and 177°C values are essentially the same (within the scatter normally obtained for tensile shear specimens).

Small flat composites were fabricated from solution-coated drum-wound prepreg using unsized AS-4 fiber. No work was conducted to optimize prepreg preparation or composite processing conditions. The initial laminates exhibited problems frequently associated with the use of drum-wound prepreg. These include fiber misalignment, non-uniform resin content and areas of poor fiber wetting. In addition, the cured composites exhibited fiber washout and a small amount of warpage. Further work will be performed in an attempt to correct these problems. The preliminary laminate properties are presented in table 3. In

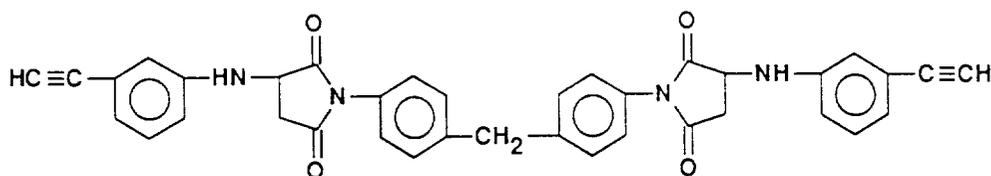
spite of the quality of the laminates, promising mechanical properties were obtained. The retention of flexural strength and modulus at 150 and 177°C after a cure for 2 hr at 250°C under [1.4 MPa (200 psi)] is particularly noteworthy. It appears that a 2 hr cure at 250°C is necessary to develop useable properties at 177°C. In addition, fracture energy of [438 J/m<sup>2</sup> (2.5 in lb/in<sup>2</sup>)] is an acceptable value.

## CONCLUSIONS

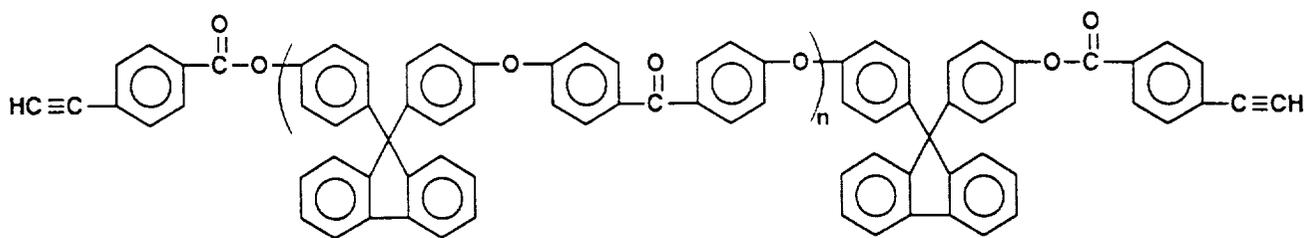
A blend of an ethynyl containing aspartimide and an ethynyl terminated arylene ether oligomer ( $M_n \sim 8000$  g/mol) was prepared, characterized and evaluated as a composite matrix. The material performed well despite problems associated with prepreg quality. Further efforts will be expended to overcome these shortcomings.

## REFERENCES

1. P. M. Hergenrother, S. J. Havens and J. W. Connell, *Polym. Prepr.* **27**(2), 408 (1986)
2. J. W. Connell, R. G. Bass and P. M. Hergenrother, *Sci. Adv. Matl. Proc. Eng. Series* **33**, 251 (1988)
3. J. W. Connell and P. M. Hergenrother, *Intl. SAMPE Tech. Conf. Series* **21**, 1029 (1989)
4. J. W. Connell, P. M. Hergenrother and S. J. Havens *High Perf. Polym. J.* **1**(2), 119 (1989)
5. P. M. Hergenrother, J. W. Connell and S. J. Havens U.S. Pat. 4,889,912 (1989) to NASA
6. J. W. Connell, R. G. Bass and P. M. Hergenrother U.S. Pat. 4,861,882 (1989) to NASA
7. J. M. Whitney, C. E. Browning and W. J. Hoogsteden, *Reinf. Plast. Composites*, **1**, 297 (1982)



Ethynyl Terminated Aspartimide (ETA)



Ethynyl Terminated Arylene Ether Oligomer (ETAE  $\bar{M}_n \sim 8000$  g/mol,  $n = \sim 15$ )

Figure 1. Chemical structure of blend components.

Table 1 - Neat Resin Properties

Property	Cure and/or Exposure Conditions			
	0.5 hr @ 250°C/200 psi	0.5 hr @ 250°C/200 psi 650 hr @ 200°C, air	0.5 hr @ 250°C/200 psi 1 X 10 <sup>9</sup> Rads (electron beam exposure)	2 hr @ 250°C/200 psi
T <sub>g</sub> , °C	245	254	254	249
Tensile St., MPa (Ksi)	93.1 (13.5)	95.8 (13.9)	76.5 (11.1)	89.0 (12.9)
Tensile Mod., GPa (Ksi)	3.6 (525)	3.9 (569)	3.9 (571)	3.55 (515.5)
Elong. (break), %	2.6	2.4	2.0	2.6
K <sub>IC</sub> , MPa m <sup>1/2</sup> (psi in <sup>1/2</sup> )	1.57 (1425)	—	—	—
G <sub>IC</sub> , J/m <sup>2</sup> (in lb/in <sup>2</sup> )	675 (3.8)	—	—	—
Coef. Therm. Expansion, ppm/°C	36.8	34.7	—	—

Table 2 - Ti to Ti Tensile Shear Strengths

Test Condition	Strength, MPa (psi) [failure mode]
23°C	22.8 (3300) (cohesive)
23°C after 650 hr @ 200°C, air	17.9 (2600) (mixed)
150°C	17.2 (2500) (cohesive)
150°C after 650 hr @ 200°C, air	20.5 (2975) (mixed)
177°C	8.3 (1200) (thermoplastic)
177°C after 650 hr @ 200°C, air	18.6 (2700) (mixed)

Table 3 - Preliminary Unidirectional Laminate Properties

Property	Cure and Exposure Conditions	Resin Content, %	Test Temperature, °C		
			23	150	177
Tensile St., MPa (Ksi)	2 hr @ 250°C/1.4 MPa	35	1917 (278)	1737 (252)	—
Tensile Mod., GPa (Msi)			121 (17.6)	139 (20.2)	—
Tensile Strain, %			1.33	1.21	—
Flexural St., MPa (Ksi)	0.5 hr @ 250°C/1.4 MPa	36	1613 (234)	683 (99)	—
Flexural Mod., GPa (Msi)			106 (15.4)	60.0 (8.7)	—
Flexural St., MPa (Ksi)	0.5 hr @ 250°C/1.4 MPa	36	1530 (222)	1323 (192)	1214 (176)
Flexural Mod., GPa (Msi)	650 hr @ 200°C, air		99.3 (14.4)	104 (15.1)	89.6 (13.0)
Flexural St., MPa (Ksi)	0.5 hr @ 250°C/1.4 MPa	36	1661 (241)	1131 (164)	—
Flexural Mod., GPa (Msi)			1 X 10 <sup>9</sup> rads	108 (15.6)	90.3 (13.1)
Flexural St., MPa (Ksi)	2 hr @ 250°C/1.4 MPa	33	1517 (220)	1462 (212)	1359 (197)
Flexural Mod., GPa (Msi)			104 (15.1)	100 (14.5)	97.2 (14.1)
Flexural St., MPa (Ksi)	2 hr @ 250°C/1.4 MPa	33	1483 (215)	1290 (187)	1124 (163)
Flexural Mod., GPa (Msi)			500 hr @ 200°C, air	102.7 (14.9)	97.2 (14.1)
Short Beam Shear St., MPa (Ksi)	0.5 hr @ 250°C/1.4 MPa	38	74.5 (10.8)	32.4 (4.7)	29.0 (4.2)
Fracture Energy (G <sub>IC</sub> ), J/m <sup>2</sup> (in lb/in <sup>2</sup> )	2 hr @ 250°C/1.4 MPa	36	438 (2.5)	—	—